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MST- $X\alpha$  CALCULATIONS ON MOLYBDENUM DISULPHIDE AND SOME RELATED COMPOUNDS

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Self-consistent-field  $X\alpha$  cluster calculations are reported for  $\text{MoS}_2$ ,  $\text{NbS}_2$  and  $\text{ZrS}_2$ . The results are compared with photoemission data. It is concluded that self-consistency and relaxation have a large effect on the relative position of the various energy levels in these compounds.

IN RECENT YEARS, molybdenum disulphide and related compounds with a layer structure have been the subject of many experimental and theoretical studies<sup>1,2</sup>. The marked anisotropy of these compounds, the superconducting properties of some of them and the possibility of intercalating metals and even organic molecules between the layers explain this interest.

The first calculations of the electronic structure of  $\text{MoS}_2$  are those of Huisman *et al.*,<sup>3</sup> who applied the Wolfsberg–Helmholtz molecular orbital method to a  $\text{MoS}_6$  cluster. Bromley *et al.*<sup>4</sup> carried out a semi-empirical tight-binding band structure calculation. More recently, an APW calculation of the band structure was reported by Mattheiss,<sup>5</sup> and a band structure calculation by Kasowski<sup>6</sup> using the L.C.M.T.O. theory. Wood and Pendry<sup>7</sup> used a modified version of the K.K.R. theory for their calculation of the band structure of  $\text{MoS}_2$ .

The calculations just mentioned were not carried out self-consistently. Self-consistency effects play a more important role in transition-metal compounds than they do in the pure metals. This is because charge transfer and back-donation can change the distribution of the outer electrons substantially with the result that the self-consistent potential can be quite different

from the potential obtained from a summation of atomic charge densities. However, it is very difficult to carry out a self-consistent band structure calculation.

In semi-empirical band structure calculations experimental data involving excited states are used to fit band structure parameters. However, this is a dangerous procedure if the effect of relaxation, which accounts for many-electron effects accompanying the electronic transition, is not taken into account. These relaxation effects affect different energy levels in a different way; they are particularly important for electrons in narrow bands and for charge transfer transitions.

The MST cluster approach<sup>8</sup> is a suitable theory for taking into account the effects of self-consistency and relaxation. The approximations in this theory are the local density approximation, the cluster approximation and the muffin-tin approximation. Of these approximations the latter is probably the most serious one.

Calculations were carried out for  $\text{MoS}_6^{8-}$  and  $\text{NbS}_6^{8-}$  in a trigonal–prismatic coordination, and for  $\text{ZrS}_6^{8-}$  in an octahedral coordination. The geometry and the interatomic distances used in the calculations for the clusters correspond to the parameters of the solid compounds  $\text{MoS}_2$  and  $\text{ZrS}_2$ . For the  $\text{NbS}_6^{8-}$  cluster the parameters for  $\text{MoS}_2$  were taken, the differences with the  $\text{NbS}_2$  parameters are negligible.

\* Calculations were performed at CECAM, "Centre Européen de Calcul Atomique et Moléculaire", Orsay, France.

Table 1 Calculated self-consistent orbital energies (in Rydbergs). The Fermi-level  $E_f$  is indicated. The  $A'_1$  level in  $\text{NbS}_6^{8-}$  at the Fermi-level is occupied by one electron

Character of wave function	$\text{ZrS}_6^{8-}$	$\text{NbS}_6^{8-}$	$\text{MoS}_6^{8-}$	Relaxation in $\text{MoS}_6^{8-}$
Beginning of hybridised conduction band	$T_{1u} = -0.530$ $A_{1g} = -0.658$	$A'_1 = -0.601$	$A'_1 = -0.594$	
Mainly metal $d$ character	$E_g = -0.415$ $T_{2g} = -0.461$	$E'' = -0.558$ $E' = -0.665$ $E_f - A'_1 = -0.715$	$E'' = -0.653$ $E' = -0.748$ $E_f - A'_1 = -0.793$	$A'_1 = -0.992$
Mainly sulphur $p$ character	$T_{1u} = -0.987$ $T_{1g} = -0.001$ $E_g = -1.004$ $T_{2u} = -1.050$ $A_{1g} = -1.093$ $T_{1u} = -1.106$ $T_{2g} = -1.118$	$A''_2 = -0.987$ $E' = -0.987$ $E'' = -0.976$ $E'' = -0.999$ $A'_2 = -1.001$ $A'_1 = -1.035$ $A'_1 = -1.112$ $E' = -1.118$ $A'_1 = -1.120$ $E'' = -1.133$ $A''_2 = -1.135$ $E' = -1.154$	$E'' = -0.969$ $A''_2 = -0.983$ $E' = -0.988$ $A'_1 = -0.994$ $E'' = -1.006$ $A'_2 = -1.031$ $A'_1 = -1.109$ $E' = -1.113$ $A'_2 = -1.129$ $E'' = -1.130$ $E' = -1.149$ $A'_1 = -1.195$	$E'' = -1.130$ $A''_2 = -1.143$ $E' = -1.151$ $A'_1 = -1.153$
Mainly sulphur $s$ character	$E_g = -1.714$ $T_{1u} = -1.725$ $A_{1g} = -1.755$	$E'' = -1.724$ $E' = -1.752$ $A'_2 = -1.767$ $A'_1 = -1.805$	$E'' = -1.709$ $E' = -1.739$ $A''_2 = -1.754$ $A'_1 = -1.793$	

The muffin-tin radii were chosen in such a way that the interstitial region was as small as possible all spheres were touching. The corresponding radii are 1.575 and 2.987 a.u. for the metal and sulphur, respectively, in  $\text{MoS}_6^{8-}$ , and 1.434 and 3.462 a.u. for zirconium and sulphur, respectively, for the  $\text{ZrS}_6^{8-}$  cluster. The charge of the cluster, which is a consequence of its non-stoichiometric composition, was compensated by surrounding the cluster by a positively charged sphere, the so-called Watson sphere. Starting potentials were obtained from a superposition of atomic charge densities, calculated with the relativistic Hartree-Fock-Slater program of Desclaux. For the coefficients  $\alpha$  in the local density approximation the values within the atomic spheres were chosen according to Schwartz.<sup>9</sup> In the regions between the atomic spheres the sum of one third of the  $\alpha$  value of the metal and two thirds of the  $\alpha$  value of the sulphur was used, and the metal  $\alpha$  value was used

in the outer-sphere region. The maximum  $l$  value used for the decomposition of the wave function into spherical harmonics was two for all spheres. It was found that spherical harmonics with  $l = 3$  did not give a significant contribution, whereas the  $l = 2$  components in the sulphur spheres had an appreciable effect. The effect of relaxation was calculated using the transition state concept due to Slater<sup>10,11</sup> for the five highest occupied levels.

The calculated orbital energies of the clusters are given in Table 1. The states are labeled according to their point group symmetry  $D_{3h}$  for  $\text{MoS}_6^{8-}$  and  $\text{NbS}_6^{8-}$ , and  $O_h$  for  $\text{ZrS}_6^{8-}$ . The absolute values of the energies for the octahedral cluster cannot be compared with the absolute values for the trigonal-prismatic clusters because of the different Watson-sphere radii.

In Fig. 1 the calculated energy levels for the  $\text{MoS}_6^{8-}$

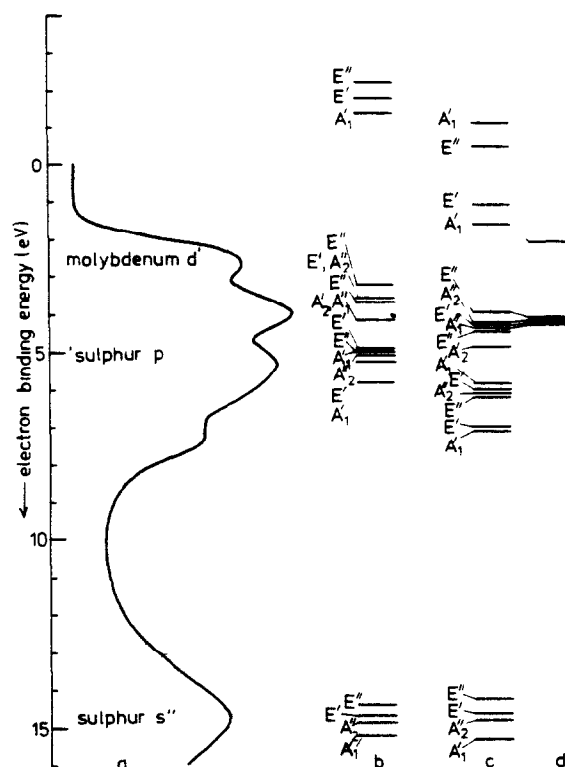


FIG 1 Energy levels of MoS<sub>2</sub> (a) Photoelectron spectra of 3R-MoS<sub>2</sub> (reference 12) (b) Non-self-consistent calculation for the MoS<sub>6</sub> cluster (c) Self-consistent calculation for the MoS<sub>6</sub><sup>8-</sup> cluster. (d) Self-consistent calculation of MoS<sub>6</sub><sup>8-</sup> including relaxation for the five highest occupied levels

cluster are compared with X-ray photoelectron spectra obtained by Wertheim *et al*<sup>12</sup> These spectra agree with photoelectron spectra using u v excitation.<sup>14</sup> For the comparison of the calculated energy levels with the photoelectron spectra the zero of energy was adjusted in such a way that the centre of gravity of the observed sulphur *s* band coincides with the calculated levels. In the calculations with relaxation the centre of gravity of the upper four "sulphur *p*" states was made to coincide with the centre of gravity of the four corresponding states in the self-consistent calculation.

At low energies there is a valence band, the lower part being essentially of sulphur *s* character, the upper part of sulphur *p* character with some molybdenum character in the states of symmetry *A*<sub>1</sub><sup>'</sup>, *E*<sup>'</sup> and *E*<sup>"</sup>. Just below the Fermi level there is a state *A*<sub>1</sub><sup>'</sup>, which has mainly molybdenum *d* character (*d*<sub>z<sup>2</sup></sub>). Above the

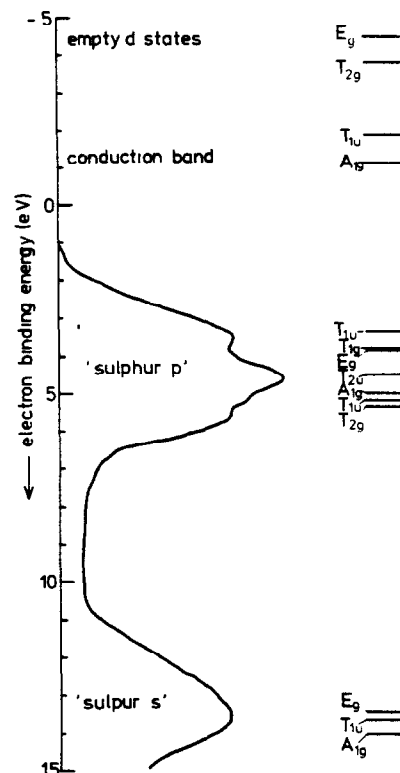


FIG 2 Energy levels of ZrS<sub>2</sub> (a) Photoelectron spectra (reference 12) (b) Self-consistent calculation for the ZrS<sub>6</sub><sup>8-</sup> cluster

Fermi level one finds two unoccupied states of molybdenum *d* character with some sulphur character. At still higher energies states of molybdenum (*s*, *p*) character and intersphere character are found.

The largest difference between theory and experiment is in the position of the occupied molybdenum *d* level *A*<sub>1</sub><sup>'</sup> with respect to the top of the valence band. Although the error is diminished substantially by the self-consistency and relaxation effects, an appreciable error remains. This is likely to be the result of the muffin-tin approximation. It is worth while noting, that for the non-selfconsistent calculation a molybdenum charge density corresponding to the neutral atom 4*d*<sup>2</sup>5*s*<sup>2</sup>5*p*<sup>2</sup> configuration was used. A non-selfconsistent calculation with the normal molybdenum 4*d*<sup>5</sup>5*s*<sup>1</sup> configuration leads to an even larger error in the position of the *A*<sub>1</sub><sup>'</sup> *d* level.

In Fig 2 the calculated energy levels of ZrS<sub>6</sub><sup>8-</sup> are compared with X-ray photoelectron spectra of ZrS<sub>2</sub>.<sup>12</sup> The photoelectron spectra of ZrS<sub>2</sub> obtained with u v

excitation are similar.<sup>13</sup> The calculation shows that the energy difference between the valence band and the  $d$  states increases from Mo to Zr and that the hybridisation of  $d$  character into the valence band decreases. This effect, together with the different type of coordination of the  $ZrS_6^{2-}$  cluster, explains the difference in ionicity between  $MoS_2$  and  $ZrS_2$ . However, the differences obtained are smaller than is suggested by i.r. data of the vibrational spectra.<sup>15</sup> A more detailed analysis of the results including a discussion of the hybridisation

of the  $A'_1 d$  state, estimates of band width and correlation effects will be given elsewhere.<sup>16</sup>

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